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(54) Title of the Invention: **Method for the Purification of Terephthalic Acid**

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SPECIFICATION

1. Title of the Invention

Method for the Purification of Terephthalic Acid

2. Claims

A method for the purification of terephthalic acid, wherein p-xylene is subjected to liquid-phase air oxidation using a heavy metal catalyst in a lower fatty acid, after which the precipitated terephthalic acid is washed using a lower fatty acid that contains or does not contain a small quantity of water, and high-purity terephthalic acid for direct polymerization is manufactured without performing a chemical treatment, said method characterized in that, after the washing operation performed using the lower fatty acid, the solid and solution are separated and the terephthalic acid cake thus obtained is further washed with water.

3. Detailed Description of the Invention

The present invention provides a method in which p-xylene is subjected to liquid-phase air oxidation using a heavy metal catalyst in a lower fatty acid, after which the precipitated terephthalic acid is washed using a lower fatty acid that contains or does not contain a small quantity of water. In this method, high-purity terephthalic acid for direct polymerization is manufactured without performing a chemical treatment, and after the washing operation, the lower fatty acid and catalyst residue that remain in the terephthalic acid are markedly reduced in content by further washing the terephthalic acid with water, so that when the terephthalic acid is provided as a raw material for the manufacture of polyesters by direct polymerization, it is possible to markedly reduce the coloration and abnormal taste brought about by the decomposition and condensation products of lower fatty acids, which are often generated and which tend to corrode the polymerization apparatus and become admixed in the polymer.

Recently, various methods for manufacturing terephthalic acid by processes in which p-xylene is subjected to air oxidation in acetic acid containing a small quantity of water in the presence or absence of a promoter using a heavy metal catalyst (JP (Kokoku) 34-2666, JP (Kokoku) 40-13856, etc.) have been implemented on a commercial scale, and the products have been widely used as raw materials for polyester fibers, films and plastics.

The terephthalic acid that is manufactured by these methods contains, in addition to p-tolu[yl]ic acid and 4-carboxybenzaldehyde (hereafter abbreviated as 4-CBA), various colored impurities that are difficult to identify. When the acid is used in unaltered form for direct polymerization, high quality polyester cannot be obtained. For this reason, a method has been implemented industrially as a process for the manufacture of high purity terephthalic acid for use in direct polymerization in which the terephthalic acid is completely dissolved in water at a high temperature and high pressure, and is then subjected to hydrogenation or is treated using a hydrogenation catalyst (JP (Kokoku) 41-16860).

Recently, methods for manufacturing high purity terephthalic acid for use in direct polymerization by simple operations whereby such complex operations are avoided have been developed and implemented industrially, and great attention has been drawn to them as methods that bring about a considerable decrease in cost (JP (Kokoku) 45-36732, JP (Kokoku) 49-25936, etc.).

Common examples of these methods include those that entail precipitating most of the terephthalic acid that is produced in the oxidation reactor by the air oxidation of p-xylene at a high temperature in hydrated acetic acid in the presence of a combination of paraldehyde and cobalt acetate or a combination of a mixed catalyst of a cobalt salt, a manganese salt, and a bromine compound. The temperature and the pressure of the resulting slurry-like reaction mixture are reduced successively in several crystallization tanks that are linked in a series, after which the solid and the solution are separated with a centrifuge or a filter, the terephthalic acid cake thus obtained is then made into a slurry again with acetic acid containing a small quantity of water, a heating and washing operation is performed under stirring at normal or increased pressure, the terephthalic acid cake is separated by solid-liquid separation, and the terephthalic acid cake is then dried (JP (Kokai) 47-390444, JP (Kokai) 48-67239, JP (Kokai) 50-83338, etc.). There are also methods in which an oxygen-containing gas is first introduced into the first crystallization tank as needed, and is then oxidized to reduce the quantity of oxidation intermediates (JP (Kokai) 51-39642, JP (Kokai) 51-16630), methods in which the washing operation is repeated several times, and methods in which another washing operation is carried out by thoroughly washing the terephthalic acid cake with acetic acid in the separator during solid-liquid separation after the crystallization tank.

The so-called medium-purity terephthalic acid that has been manufactured in this procedure, in addition to containing 200 ppm to several hundred parts per million of 4-CBA, contains only an extremely small quantity of colored substances. It is well known that high quality polyester filaments, staple fibers, films and engineering resins can be manufactured in the same manner as so-called purified terephthalic acid that has been hydrogenated or treated using a hydrogenation catalyst.

However, this high purity terephthalic acid, in addition to inevitably containing 100 to 200 ppm of acetic acid, also contains bromine compounds in an amount 10 to 100 times that of the purified terephthalic acid. That is, 2 to 30 ppm of bromine compounds as bromine atoms remain together with numerous other impurities, although in amounts far less than that of the purified terephthalic acid.

When these impurities are present, they have essentially no effect on the quality of the terephthalic acid that is produced. However, they gradually accumulate in the ethylene glycol recovery system and corrode it. Further, when such polymers are used in the manufacture of

bottles for carbonate beverages, to which particular attention has arisen in recent years, it has been discovered that there are instances in which an irritating taste is unexpectedly presented. This taste is presumably caused by the corrosion brought about by the bromine compounds and acetic acid contained in medium-purity terephthalic acid. It is also presumed that the irritating odor is sometimes caused as a result of the fact that acetic acid is decomposed and condensed by the treatment under high temperatures in the polymerization reaction, and the resin-like substance that is produced is admixed in the polyester polymer. However, the true cause has not yet been found.

The inventors, by washing with water the so-called medium-purity terephthalic acid cake obtained by solid-liquid separation after acetic acid washing, easily removed the acetic acid and residual bromine compounds contained in the terephthalic acid, making it possible to inhibit the corrosion of the polymerization apparatus and the irritating taste of beverages contained in polyester bottles made from the polymer, and succeeding in eliminating these drawbacks to a degree at which they can be essentially ignored.

Washing is performed with water that contains essentially no acetic and bromine compounds.

The washing operation can be performed by washing the terephthalic acid cake in the separator with water at the time of solid-liquid separation after the acetic acid washing. Washing can also be performed by again making the cake into a slurry with water, stirring the slurry, and separating the terephthalic acid by solid-liquid separation.

The water temperature can range from normal temperature to 160°C, and the pressure can be normal pressure or an increased pressure within a range in which water is maintained in liquid state.

The amount of water relative to the terephthalic acid should be in a range of 0.5 to 10 times the weight of the acid, with 1 to 3 times the weight of the acid being most desirable.

We shall now describe the invention by means of a working example. It is apparent that the present invention is not limited to the scope of the working example alone.

Working Example

p-Xylene was oxidized by air at 190°C and 20 kg/cm² in an acetic acid solution in the presence of a mixed catalyst of cobalt acetate, manganese acetate and hydrogen bromide, after

which the oxidation product was subjected to a follow-up oxidation treatment in the first crystallization tank at 140°C in dilute air containing 8% of oxygen. Solid-liquid separation was then performed in the second crystallization tank with a centrifuge set to normal pressure. The product was then washed and subjected to solid-liquid separation with three times its weight of acetic acid at 150°C and an increased pressure of 6 kg/cm². 100 parts of terephthalic acid, which contained 10% of acetic acid, 300 ppm of 4-CBA and 35 ppm as bromine atoms relative to the terephthalic acid, was introduced together with 250 parts of water into a vessel equipped with a stirrer, the system was stirred at 50°C for 30 minute and a rotational speed of 300 ppm [sic], and the product was separated and dried with a centrifuge. The terephthalic acid that was produced contained 300 ppm of 4-CBA, 2 ppm of acetic acid and no more than 1 ppm of bromine compounds as bromine atoms. The acid was then used in direct polymerization, and high-quality polyester was obtained. There was no corrosion of the apparatus, and when the polymer sheet was immersed for 1 week in a carbonated beverage, no abnormal taste whatsoever was acquired by the beverage. When the product was not washed with water, terephthalic acid containing 300 ppm of 4-CBA, 130 ppm of acetic acid and 35 ppm of bromine compound as bromine atoms was obtained. When the polymer sheet was immersed for 1 week in a carbonated beverage, the carbonated beverage acquired a slightly irritating taste.

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